

STATUS AND OVERVIEW OF THE DOE-FUNDED PROJECTS RELATED TO  
CHEMICAL GAS STREAM CLEANUP PROGRAM

Daniel C. Cicero  
Suresh C. Jain

Department of Energy  
Morgantown Energy Technology Center  
P.O. Box 880  
Collins Ferry Road  
Morgantown, West Virginia 26505

INTRODUCTION

The U.S. Department of Energy has undertaken a Chemical Gas Stream Cleanup Program to simplify and improve methods for cleaning gas generated from coal either by gasification or combustion. The projects which comprise this development program are mainly aimed at gas streams generated at pressures greater than 6 atmospheres and temperatures greater than 1,000°F. These elevated pressures and temperatures would be associated with emerging technologies such as integrated gasification combined-cycle molten carbonate fuel cell power plants, direct-fired coal turbines, and pressurized fluidized-bed combustion. Control and removal of the contaminants is a technical limitation and a major cost associated with these advanced coal utilization systems.

The overall program objective is to develop technologies economically to remove hot gas stream contaminants such as sulfur compounds, nitrogen compounds, alkalis, selected trace metals, and residual hydrocarbons which are detrimental to advanced coal-fired systems (1). Selection and continuance of the projects is based on their ability to meet performance and environmental requirements and to show promise of significant cost reduction over available technologies.

The Department of Energy through the Morgantown Energy Technology Center (METC) carries out development programs for many of the other fuel conversion and power-generating components for advanced energy systems based on coal. Besides the Gas Stream Cleanup Program, METC implements programs in Gasification, Heat Engines, Fuel Cells, Fluidized-Bed Combustion, Components, and Solid Waste Management. A high degree of coordination with these programs is maintained to insure compatibility and proper integration of development efforts. Figure 1 depicts the integration of Chemical Gas Stream Program.

DISCUSSION

The products of coal gasification or combustion contain contaminants which were part of the coal feedstock. These contaminants include sulfur compounds, chlorides, nitrogen compounds (HCN, NH<sub>3</sub>, NO<sub>x</sub>), alkalis, particulates, and trace elements. Removal of the sulfur and nitrogen compounds and the particulates is necessary to meet national air quality standards for SO<sub>2</sub>, NO<sub>x</sub>, and suspended solids. Removal of the other contaminants is required for some applications to avoid equipment damage or serious degradation in performance. In particular, gas turbines have a very low tolerance for alkali compounds and molten carbonate fuel cells (MCFC) for sulfur compounds. The fuel cell sulfur limit is well below the environmental requirements for sulfur control. The effect of sulfur on cell operation has been studied both theoretically and experimentally. The results from the Institute of Gas Technology (2), United Technologies Corporation (3), and General Electric (4) work indicate that sulfur present in either the anode or cathode feed affects the performance of the nickel anode.

The cleanup requirements for four applications (pressurized fluidized-bed combustion/turbine, integrated gasification combined-cycle, molten carbonate fuel cell, and direct coal-fired turbine) and six categories of contaminants (particulates, sulfur, alkali, nitrogen, trace metals, and chlorine) are given in Table 1. Two applications pertain to cleanup of products of combustion before entering a turbine, one application is for low-Btu gas for turbine use and one is for medium-Btu gas for fuel cells. Allowable level of particulates for the pressurized fluidized-bed combustion/turbine and integrated gasification combined-cycle applications are in the range of  $1.7 \times 10^{-4}$  to 0.01 grain (gr) per standard cubic feet (scf) and  $4.1 \times 10^{-3}$  to 0.24 gr per scf, respectively.

The DOE Chemical Gas Stream Cleanup program has centered on matching of cleanup subsystem temperature and pressure to that required by the end use process element and the upstream gasifier or combustor. This matching should provide attractive systems by eliminating heat recovery equipment and compressors or expanders. Figure 2 shows a temperature-pressure plot with various subsystems in their operating envelopes. With gasifier turbine power systems, an ideal match is achieved with fixed-bed gasifiers and a zinc ferrite desulfurization subsystem. This combination of gasifier and hot cleanup has been referred to as a "gasification island" concept by METC and has been receiving high priority in development. Molten carbonate fuel cells operate at about the same temperatures but at lower pressures than gas turbines; both the zinc ferrite subsystem and some novel sorbent subsystems would be an ideal temperature match. A relatively unknown area is that required for direct-fired turbines where temperatures can range from 2,000° to 2,800°F or higher. Although a temperature-pressure match is attractive, systems analysis is necessary to examine all factors that effect performance and cost.

The Chemical Gas Stream Cleanup Program, as shown in Figure 3, is divided into six contaminant removal areas, i.e., sulfur, alkali, tars, trace species, chloride, and nitrogen. Each removal area is briefly discussed below. Particulate removal is a separate project area pursued by METC and is not discussed in this presentation.

#### Sulfur Removal

The need to comply with environmental standards makes sulfur removal important for all coal gas applications. However, MCFC applications require sulfur levels below the 1 part per million (ppm) range (5), while other applications allow 100 ppm or more. Nevertheless, sulfur removal to below 10 ppm could be beneficial for turbine applications, because sulfur and alkalis interact to cause corrosion and/or deposition on turbine blades, and reducing sulfur may allow less stringent alkali removal requirements. Projects under sulfur removal are shown in Figure 4.

Figure 5 shows sulfur removal technologies for various temperatures of fuel gas. Many cold scrubbing technologies are available for removing fuel gases up to temperatures of about 350° to 400°F. These techniques can achieve very high sulfur removals if designed in stages with extensive recycle. For fuel gas temperatures from about 850° to 1,200°F, two systems have shown promise: an iron oxide sorbent and a zinc ferrite sorbent. Iron oxide was tested at METC in the 1970's on fuel gas from a fixed-bed gasifier. These tests showed feasibility of the sorbent for achieving up to 90 percent sulfur removal. IHI subsequently has been testing this process on a pilot scale.

Recent development work at METC has shown zinc ferrite to be a likely candidate for hot gas desulfurization, because it can remove all sulfur species in the gas to below 5 ppm except for that found in the tar. Five projects are underway to explore the questions that remain in zinc ferrite sorbent development. In addition, the zinc ferrite absorber will be scaled up and tested at the process development unit (PDU) fluidized-bed gasifier at the KRW Energy Systems, Inc., Waltz Mill site early in 1986.

TABLE 1

Allowable Level of Contamination in Cleaned Gas for Four Potential Commercial Applications

	Pretreated Fluidized-Bed Combustion/Turbine (Products of Combustion)	Integrated Gasification Combined Cycle (g) (Low-Btu Gas)	Hot-Side Carbonate Fuel Cell (Medium-Btu Gas) (d)	Direct Coal-Fired Turbine (Products of Combustion)
1. Particulates	.004 gr/scf <sup>(b)</sup> , NSPS for Coal-Fired Boiler	.106 gr/scf, NSPS for Coal-Fired Power Generation	TBD <sup>(e)</sup> .0056 PPM Weight <sup>(9)</sup>	TBD <sup>(e)</sup>
	3.2 x 10 <sup>-4</sup> gr/scf, Brown-Boveri <sup>(7)</sup>	.0077 gr/scf, Brown-Boveri <sup>(7)</sup>		
	1.7 x 10 <sup>-4</sup> gr/scf, General Electric <sup>(7)</sup>	.0041 gr/scf, General Electric <sup>(7)</sup>		
	2.2 x 10 <sup>-4</sup> gr/scf, United Technologies	.0053 gr/scf, United Technologies		
	.002 gr/scf, Westinghouse <sup>(8)</sup>	.048 gr/scf, Westinghouse <sup>(8)</sup>		
	.01 gr/scf, HETC Proposed <sup>(1)</sup>	.24 gr/scf, HETC Proposed <sup>(1)</sup>		
		.01 gr/scf, Westinghouse Blast Furnace Gas <sup>(8)</sup>		
2. Sulfur	269 PPM <sup>(10)</sup> , NSPS for Coal-Fired Boilers	1616 PPMV, NSPS for Turbines <sup>(10)</sup>	.1-1 PPMV H <sub>2</sub> S + COS <sup>(11)</sup>	269 PPMV <sup>(10)</sup> for Gas Turbines <sup>(b)</sup>
	101 PPMV, NSPS for Coal-Fired Power Generation (98% Reduction) <sup>(15)</sup>	606 PPMV, NSPS for Coal-Fired Power Generation (90% Reduction) <sup>(16)</sup>	1 PPMV <sup>(9)</sup>	101 PPMV, NSPS for Coal- Fired Power Generation <sup>(1)</sup> (90% Reduction) <sup>(18)</sup>
3. Alkalies <sup>(c)</sup>	.0063 - .063 PPMV <sup>(f)</sup>	.05 - .5 PPMV <sup>(f)</sup>	TBD <sup>(e)</sup>	TBD <sup>(e)</sup>
	.02 PPMV, GE Proposed <sup>(1)</sup>	.2 PPMV, HETC Proposed <sup>(1)</sup>		May Be Same as PFBC
4. Nitrogen NO <sub>x</sub> Low	None; Low Bed Temperature Should Keep NO <sub>x</sub> Low	25 PPMV, HETC Proposed to Meet NO <sub>x</sub> Standards <sup>(1)</sup>	TBD <sup>(e)</sup> None <sup>(9)</sup>	25 PPMV, HETC Proposed to Meet NO <sub>x</sub> Standards <sup>(1)</sup>
5. Trace Metals	V.0063 - .025 PPMV <sup>(f)</sup> Ca = .125 PPMV <sup>(f)</sup>	V.05 - .2 PPMV <sup>(f)</sup> Ca = 1 PPMV <sup>(f)</sup>	TBD <sup>(e)</sup>	TBD <sup>(e)</sup>
6. Chlorine	None <sup>(8)</sup>	None <sup>(8)</sup>	.1 - 1 PPM <sup>(11)</sup> 10 PPM HCl <sup>(9)</sup>	None <sup>(8)</sup>

(a) Particulates, alkalis, and trace metals are back-calculated from PFBC. Assumptions: 160 Btu/scf gas; air/gas to turbine, 5.0 (1,333°F heat rise); particulates are 75% carbon, which is consumed ahead of turbine inlet; cold gas efficiency of gasifier is 80%.

(b) Particulates are 75% carbon, which is consumed ahead of turbine inlet; cold gas efficiency of gasifier is 80%.

(c) Varies with air/coal ratios; coal MBV.

(d) Tolerances for alkali removal are expected to be much higher if sulfur removal is 10 PPMV.

(e) To obtain tolerances for low-Btu gas, divide by 2.

(f) To be determined; tolerances are either unknown or are not firm. Contracts planned or in place to determine tolerances.

(g) Manufacturers standards for fuel oil fired turbines (8).

38-3-28-85:pb:49

Another category of sorbents referred to as mixed metal oxide and novel sorbents has been under investigation. These sorbents have promise of achieving desulfurization at higher temperatures and potentially producing elemental sulfur on regeneration. The Institute of Gas Technology (IGT) mixed metal oxide process and Battelle Pacific Northwest Laboratories solid supported molten salt process are currently at the bench-scale development stage. In addition, Jet Propulsion Laboratories (JPL) is completing laboratory-scale tests on entirely new types of synthesized sorbents; the most promising sorbents will be tested at the bench scale late in 1986.

At temperatures from 1,500° to about 2,000°F, calcium-based sorbents have been tested and achieved over 95 percent sulfur removal. These processes are not currently being developed by DOE. Earlier work by CONOCO and others have shown the feasibility of these systems. METC is exploring the potential of combining sulfur removal with gasification processes, however, in tests in a fluid-bed gasifier under the METC gasification program.

The final determination of which of these processes will find use in sulfur removal systems will depend on economics. Two pieces of these economic studies are being carried out by Gilbert/Commonwealth, Incorporated, in studies of reactor costs, and Ralph M. Parsons Company in evaluations of tail gas treating systems.

#### Zinc Ferrite Studies

A sulfur sorbent utilizing zinc ferrite has been under development at METC for the past 5 years. Initial tests were with gas mixtures that approximated gasifier fuel gases. Bench-scale evaluation in actual coal gas streams were then carried out and demonstrated that in the operating regime 1,000° to 1,200°F, 120 to 240 psig, and 1,000 to 2,000 h<sup>-1</sup> space velocity, a zinc ferrite sorbent can function in a hot gas stream from a fixed-bed coal gasifier, removing low molecular weight sulfur compounds to a level of about 10 ppm. High molecular weight sulfur compounds, which are in tars, however, are not removed. The sorbent picks up about 30 percent of its weight in sulfur before breakthrough. It can be regenerated by air and steam mixtures at 1,400° to 1,500°F, to near its original condition with a residual sulfur content (as sulfate) of less than 1 weight percent. Absorption performance after three regenerations is close to that of fresh sorbent (6). Figure 6 is a plot of the exit hydrogen sulfide (H<sub>2</sub>S) level attained over three cycles of absorption and regeneration. It can be seen that the H<sub>2</sub>S level is about 1 to 5 ppm before breakthrough and there is no significant drop in the sorbent sulfur loading following regeneration.

Potential improvements which may be made to the zinc ferrite system include (a) understanding metal phase changes occurring at certain operating conditions which could degrade sorbent integrity and performance; (b) minimize sulfate formation, which can occur in gases with significant SO<sub>2</sub>; and (c) reduce catalyst degradation which occurs with repeated cycling leading to reduced structural strength and loss of integrity and performance. Several contracted efforts are aimed at these improvements.

Louisiana State University is studying structural changes in hot metal oxide sorbents including zinc ferrite through adsorption and regeneration cycles. Results to date indicate that the relatively simple model is adequate to describe the time-conversion data. During most of the reaction, product layer diffusion appears to be the controlling resistance. Early in the reaction, before the product layer is fully developed, mass transfer is believed to be important.

SRI International is performing theoretical and empirical studies of phase boundaries of zinc ferrite during adsorption and regeneration. The Fe<sub>3</sub>O<sub>4</sub>/Fe, Fe<sub>3</sub>O<sub>4</sub>/wustite, carbon deposition, and carbide formation phase boundary compositions have been calculated for total pressures of 1, 5, 10, 15, and 20 atm at temperatures of 930°, 1,020°, 1,100°, 1,200°, and 1,300°F. Another SRI International study deals with sulfate formation and how it can be avoided. Fixed-bed reactor experiments were conducted at

SRI to determine the amount of sulfate formed as a function of several process variables. Higher sorbent temperature and lower oxygen partial pressure in the feed gas lead to a decrease in the amount of sulfate remaining in the regenerated sorbent is a function of duration of regeneration; longer duration decreases the amount of residual sulfate. An increase in space velocity was found to decrease the sulfate formation. In the range of particle size from 0.5 to 5 mm, the sulfate formation was not affected by the particle size. The presence of  $\text{SO}_2$  in the feed gas significantly promotes the sulfate formation.

AMAX, Incorporated, is studying how to maximize zinc ferrite physical strength and durability during the sorbent fabrication process. A sorbent which was formulated with bentonite as a binder has shown improved physical and chemical performance over the United Catalyst, Incorporated (UCI), zinc ferrite composition used in testing at METC. The AMAX sorbent had shown double the physical crush strength and twice the sulfur bearing capacity of the UCI sorbent. During the desulfurization testing, the AMAX sorbent showed the capacity for retaining its initial surface area whereas the UCI sorbent showed some loss of surface area through sintering. The AMAX sorbent also had less fines attritioning during the desulfurization testing.

#### Novel Fuel Gas Sorbents

Novel sorbents can offer higher temperature applications and simpler tail gas treatment. The Battelle solid supported molten salt (SSMS) system, under development since 1974, is at the bench-scale development stage and features both sulfur compounds and HCl removal from 6,000 ppm and 200 ppm to less than 1 ppm level, respectively. The SSMS sorbent consisted of porous lithium aluminate ceramic pellets loaded with low-calcium salt ( $\text{Li}_{1.1}\text{K}_{0.7}\text{Ca}_{0.1}\text{CO}_3$ ). The sorbent can be regenerated with carbon dioxide-steam mixture to produce a hydrogen sulfide-rich gas from which elemental sulfur could be efficiently recovered. The IGT mixed metal oxide system, under development since the late 1970's, employs two sorbents. One sorbent, cobalt titanate, removes 70 percent of the sulfur and can be regenerated with  $\text{N}_2/\text{O}_2/\text{SO}_2$  mixtures to produce elemental sulfur. The other oxide is one of many suitable for removing sulfur compounds to low levels which can be regenerated with air and steam or nitrogen to produce  $\text{SO}_2$ . Major examples are zinc oxide, iron oxide, and copper oxide.

The current research program conducted at JPL aims at synthesizing high-temperature sulfur removal sorbents that combine several desirable physicochemical properties. Certain mixed oxide sorbents have been developed with rapid kinetics of absorption and good sorbent regenerability at 930° to 1,300°F. The rapid absorption rates are realized by eliminating or minimizing the resistance associated with solid state diffusion. In one class of sorbents, stable high surface area can be obtained by eutectic mixtures of metal oxide sorbents (e.g.,  $\text{ZnO}\cdot\text{V}_2\text{O}_5$ ,  $\text{CuMoO}_4$   $\text{MoO}_3$ ), which form a melt that coats the pore surface of a high surface area support. The other class of sorbents considered in this work consists of unsupported mixed oxides forming highly dispersed solid solutions or solid compounds (e.g.,  $\text{ZnFe}_2\text{O}_4$ ,  $\text{CuFe}_2\text{O}_4$ ,  $\text{CuFeAlO}_x$ ,  $\text{CuMoAlO}_x$ ), characterized by their small crystalline size, high porosity and relatively high surface area. All sorbents exhibit high sulfur removal efficiency, stable conversion, minimal pore plugging, and good regenerability.

#### Direct-Fired Turbine Sorbents

Physical Sciences, Inc. (PSI) is undertaking a combined theoretical and bench-scale experimental program to study the feasibility of using micronized coal and coal-water mixtures (CWM) as fuels in heat engines. This project addresses two major interrelated consequences arising from the introduction of these fuels into gas turbine combustors. The first is the release of coal-bound mineral matter into the combustion product stream. A second consequence of firing coal is the emissions of sulfur oxides which have been identified as precursors to acid rain. PSI will quantify sulfur and alkali removal rates by solid sorbents and will determine the effects of the

sorbents on deposition. Westinghouse Research and Development Center will develop information on the feasibility of using limestone and dolomite sorbents for sulfur capture in post-combustion gas streams under temperature and pressure conditions typical of direct coal-fired turbine operation. Both of these projects are in early stages with findings not at a stage to report.

#### Economic System Studies

While various types of sulfur removal systems are in various stages of development, Ralph M. Parsons Company and Gilbert/Commonwealth, Incorporated, are conducting studies for cost optimization of the sulfur removal technology in a plant complex to produce 100 megawatts of electrical power. The Gilbert study focuses on various coal gasifier and fixed-/fluidized-bed sulfur absorber and sorbent regeneration systems using the Morgantown Energy Technology Center's zinc ferrite process, the Institute of Gas Technology's metal oxide process, and the Battelle Pacific Northwest Laboratory's solid-supported molten salt process. This study includes 11 cases for gasifier, hot gas cleanup, and regeneration system configurations as summarized in Table 2. The Parsons study deals exclusively with state-of-the-art sulfur recovery from regeneration gases. This study includes 11 process configurations as summarized in Table 3. Both of these studies are in the early stages and conclusions have not been reached concerning them.

#### Alkali Removal

Presence of alkali metal is a major concern in gas turbines, which operate at temperatures of 1,800°F and higher. Allowable levels of alkali metals in expansion gases for turbines to prevent corrosion or deposition on blades, stators, and rotors can be readily derived from standards for alkali content for liquid turbine fuel (.5 to 5 ppm). These standards correspond to a .05 to .5 ppm allowance for alkali metals in low-Btu gas. Encouraging results were achieved in measurements of alkali levels during a test at the General Electric Company gasifier in November 1984. The gasifier is a stirred-bed operated in an air-blown mode. Cleanup consisted of a single cyclone. Alkali levels were measured, less than 1 ppm, and approximated that calculated from alkali content in the feed coal ash.

Alkali metal tolerances for MCFC applications have not been established. A study ongoing by Energy Research Corporation (ERC) to determine the effect of trace metals on fuel cells will establish alkali tolerances if in fact they are needed. Figures 7 and 8 show the work being conducted in the areas of fundamental studies, alkali measurement, and alkali control.

Fundamental studies of release mechanisms, capture mechanisms, and fate of alkali metals are being conducted by METC, Midwest Research Institute, and the University of Arizona. Aerodyne Corporation is updating and modifying a computer model for inter-phase condensation of alkali metals in pressurized fluidized-bed combustion processes.

Three methods of alkali metal control are each being explored by Westinghouse, Argonne National Laboratory, and the University of Pittsburgh. The Argonne study is aimed at PFBC applications, the Westinghouse study is directed at pressurized coal gasification applications, while the University of Pittsburgh study is concerned with products of entrained gasification using solid collectors to trap contaminant species.

#### Fundamental Studies

A University of Arizona study is investigating the formation of alkali metal vapor in entrained flow gasification and combustion at various temperatures, and the potential for capture of these vapors with powdered kaolite or limestone. Midwest Research Institute is studying fundamental combustion chemistry in PFBC applications with the goal of verifying predictability of alkali metal concentrations in off gases by existing computer models. One such model, the PACKAGE code, is being modified, upgraded, and more fully documented by the Aerodyne Corporation.

TABLE 2. Summary of Hot Gas Cleanup Cases Studied  
by Gilbert/Commonwealth, Incorporated

Cases			Gasifier	Hot Gas Cleanup Reactor	Sulfided Sorbent Regenerator
Sorbent Process					
METC <sup>a</sup>	Battelle <sup>b</sup>	IGI <sup>c</sup>			
1	6	9	Air -- Fixed-Bed Dry Ash	Fixed	Fixed
2	7	10	O <sub>2</sub> -- Texaco Quench	Fixed	Fixed
3	8	11	O <sub>2</sub> -- Westinghouse Fluid Bed	Fixed	Fixed
4			O <sub>2</sub> -- Westinghouse Fluid Bed	Fluid	Fluid
5			O <sub>2</sub> -- Fixed-Bed Dry Ash	Fixed	Fixed

<sup>a</sup> Zinc ferrite.

<sup>b</sup> Solid-supported molten salt.

<sup>c</sup> Mixed metal oxides.

TABLE 3. Summary of Configurations of 11 "Short-List" Process  
Candidates Assessed by The Ralph M. Parsons Company

Candidate Process Grouping No.	Case No.	SO <sub>2</sub> Recovery/ Concentration Process	Sulfur Reduction/ Production Process	Tail Gas Process
1	1A	Wellman-Lord	Resox	BSR/Claus
	1B	Wellman-Lord	Resox	Recycle to W-L
	1C	Wellman-Lord	Resox	BSR/MDEA
	1D	Wellman-Lord	Resox	BSR/Stretford
2	2A	Wellman-Lord	Allied Chemical (2 Claus Stages)	None
	2B	Wellman-Lord	Allied Chemical (2 Claus Stages)	Recycle to W-L
	2C	Wellman-Lord	Allied Chemical (3 Claus Stages)	None
3	3	Wellman-Lord	Beavon Sulfur Removal (BSR)	Stretford
4	4A	Wellman-Lord	Modified Claus	BSR/Selectox
	4B	Wellman-Lord	Modified Claus	BSR/Stretford
	4C	Wellman-Lord	Modified Claus	Recycle to W-L

BSR -- Beavon Sulfur Removal.

W-L -- Wellman-Lord.

MDEA -- Methyl-di-ethanol-amine.

## Alkali Measurement

In addition to fundamental studies and development of control technology, Ames National Laboratory has developed an on-line alkali measuring device, which was further developed by METC to be capable of measuring alkali content to 10 ppb. The meter has been successfully tested at the process development unit (PDU) scale at METC and at GE Research Center, Schenectady site. The meter will be used to measure the alkali levels at the PDU scale at KRW Energy Systems, Inc., Waltz Mill site.

## Alkali Control

Westinghouse, Incorporated, has conducted research into the alkali-gettering concept since October 1978. The results of their work and that of others like Argonne National Laboratories (ANL) led to the conclusion that a fixed bed of cylindrical pellets, 1/8 inch in diameter by 1/4 inch long, of emathlite, a fuller's earth, is the best method of hot gas removal of alkali metals from products of coal gasification. Current development is at bench scale.

A recent 100-hour test conducted by Westinghouse using a shallow packed bed showed a range of 2.0 to 4.2 weight percent capture of sodium by the emathlite. The feed gas sodium concentration was reduced from 10 ppm to approximately 2 ppm. In laboratory tests at Argonne, activated bauxite shows a similar ability for sodium capture, but has the additional advantage of being regenerable via water leaching.

ANL has pioneered the development of granular sorbents suitable for use in a granular bed for the removal of alkali vapor from hot PFBC flue gas. After extensive screening of potential candidate sorbents, activated bauxite and diatomaceous earth were found to be the most effective sorbents in capturing NaCl, KCl, and K<sub>2</sub>SO<sub>4</sub> vapors from a simulated hot PFBC flue gas at atmospheric pressure.

In recent laboratory-scale, fixed-bed sorption studies at ANL, performed at conditions that closely simulate the actual PFBC flue gas (temperature, 1,560°F; pressure 10 atm absolute; gaseous composition, 3 percent O<sub>2</sub>, 16 percent CO<sub>2</sub>, 5 percent H<sub>2</sub>O, 250 ppmV SO<sub>2</sub>, few ppmV NaCl vapor, and the balance N<sub>2</sub>), NaCl-vapor removal efficiencies greater than 99 percent were achieved for both activated bauxite and diatomaceous earth sorbents. It was also demonstrated that activated bauxite can be easily and effectively regenerated for reuse by a simple water-leaching process. A preliminary evaluation indicated that the fixed granular-bed filter concept for the control of alkali vapors from PFBC flue gas is economically attractive.

A research project has been initiated at the University of Pittsburgh whose objective is the control of emissions of alkali metals, trace metals, and aromatic hydrocarbons that occur in advanced coal conversion processes such as pulverized coal combustion for turbine applications. The process is the adsorption of the undesirable components onto the surface of a solid collector, such as pulverized alumina, which is injected into the flame mixed with the feed coal. The particle size of the collector will be such that it can be easily removed from the flue gas by a cyclone or other separator.

## Tar Removal

The problem of removing tar and other lighter hydrocarbons from hot coal gas streams is of interest primarily for integrated coal gasification/molten carbonate fuel cell power plant applications using fixed-bed gasifiers. These hydrocarbons also carry a nontrivial fraction of sulfur which could impact the performance of the molten carbonate fuel cell. Tar removal is irrelevant for gas turbine use, and tar and all but the lightest hydrocarbons are absent from products of other than fixed-bed gasifiers. Figure 9 shows the work being conducted in the area of tar removal.

The Chemical Gas Stream Cleanup Program includes a study by Washington State University on the fundamentals of tar formation in fixed-bed gasifiers and preliminary

development of three broad approaches to cracking hydrocarbons in hot product gas streams from fixed-bed gasifiers by Battelle Pacific Northwest Laboratory (Battelle), Physical Sciences, Incorporated (PSI), and Massachusetts Institute of Technology (MIT).

#### Fundamentals of Tar Formation and Removal

Tars and lighter hydrocarbons appear in the raw product gas streams of fixed-bed gasifiers because conditions at the top of the bed of coal permit coal to devolatilize, but the products of devolatilization only partially break down. The type and yields of tars and lighter hydrocarbons from fixed-bed gasifiers at various conditions and the subject of coal devolatilization in general has been studied rather extensively. A METC-sponsored study by Washington State University will provide a compilation of fundamental facts about tar formation in fixed-bed gasifiers and their destruction by catalytic or thermal cracking. The study also includes empirical work to fill in gaps in information required to design MCFC power plants incorporating methods of eliminating tars from the fuel cell feed gases. Also, studies sponsored by the DOE gasification program are providing new data on tar formation mechanisms.

#### The Effects of Tar and Other Contaminants on Fuel Cell Performance and Life

Previous studies have shown particulates, soot, hydrocarbons, and trace elements to be potentially deleterious to MCFC performance and life. Soot formation is an important concern for efficient utilization of coal gas in MCFC systems. Coal gas is generally formed at temperatures greater than the MCFC operating temperatures ( $\sim 1,830^{\circ}\text{F}$  for a gasifier compared with  $\sim 1,200^{\circ}\text{F}$  for MCFC) and tends to deposit carbon in the fuel cell unless its gas composition is properly "stabilized," and the surfaces and the conditions that promote carbon deposition are minimized. The presence of hydrocarbons, tars and oils, etc., can further aggravate this problem. The effect of particulate matter present in coal gas (even after various cleanup steps) has not been characterized so far, except for some theoretical modeling under a Westinghouse/Energy Research Corporation (ERC) study performed for METC. Similarly, only some thermodynamic calculations have been performed on the possible effects of ammonia, arsenic, and other trace elements. A very limited amount of experimental data is available on the possible effects of these contaminants.

#### Tar Cracking

Three preliminary development projects at Battelle, PSI, and MIT for tar removal sponsored by METC involve the use of a cracking catalyst. Since sulfur removal to below 1 ppm is required for MCFC, a preliminary goal is to remove a sufficient quantity of tar and/or desulfurize the remaining tar so that the tar sulfur content does not prevent achievement of desulfurization requirements. The Battelle study is directed to convert the sulfur in the tar to a form (such as  $\text{H}_2\text{S}$ ) which can be removed by a hot gas desulfurization process. The results of the catalytic cracking of coal tars are shown in Figure 10. The PSI study is aimed at in-process destruction of aromatic hydrocarbons, while the MIT study is concerned with quantitative understanding of the thermal reactions of aromatic contaminants with calcium oxide.

#### Trace Species Removal

A research program in support of a high-temperature process for the removal of sulfur and arsenic containing compounds as well as other trace contaminants from coal-derived fuel gas was initiated at ERC. The process to be explored utilizes a nickel sorbent system which may be regenerable with steam and hydrogen or oxygen. This concept is supported by the fact that nickel has a strong affinity for both sulfur and arsenic even at low concentrations ( $< 10$  ppm). Both the contaminants are known poisons for the nickel catalysts. The adsorption of sulfur on nickel occurs by reversible dissociative chemisorption. A number of studies indicate that a gas stream can be purified

to very low levels of sulfur with a nickel-based catalyst, which may be regenerable as well. Figure 11a shows the work being conducted in the areas of trace species control and measurement.

#### Chloride Removal

Chloride removal to .1 to 10 ppm has been established as a requirement for MCFC applications. Requirements for other applications have not been established, but they are not expected to be as stringent. SRI International is developing a laboratory-scale process to remove HCl to below 1 ppm. Figure 11b shows the work being conducted in the area of chloride removal.

#### Nitrogen Removal

Most of the ammonia emitted from a typical gas producer has been determined to come from the reduction of the nitrogen in the fuel. The temperature-pressure relationships in an atmospheric or low-pressure gas producer are sufficient for the breakdown of ammonia in the presence of a catalyst. A large number of such catalysts have been manufactured and tested. In general, these catalysts tend to be expensive and susceptible to irreversible poisoning by hydrogen sulfide ( $H_2S$ ). Previous experimental work has indicated that the irreversible poisoning of the catalyst could be avoided by removing the  $H_2S$  from the producer gas prior to exposure to the catalyst. It has also been suggested that combining these catalysts with the fuel in the gasifier would avoid contact of the evolving  $H_2S$  gas with the catalyst and achieve the desired reduction.

A project will soon be initiated to explore both methods of ammonia decomposition, develop preliminary process economics, and make some preliminary determinations of their applicability to full-scale coal-powered gasification systems.

#### CONCLUSION

The results obtained from the ongoing DOE-funded projects related to the chemical gas stream cleanup are encouraging. The design data will be available for process engineers to develop hot gas desulfurization/regeneration systems design using zinc ferrite as the sorbent. Novel sorbents have been identified for potential removal of  $H_2S$ , COS, and HCl to less than 1 ppm.

An alkali meter has been developed which can be used wherever on-line measurements of trace alkali metal concentration in hot dirty gas or combustion product streams are required. Alkali sorbents have also been identified to remove alkalis to very low levels when required. Promising results have been obtained using the novel sorbents to convert the sulfur in the tar to hydrogen sulfide which can be removed by a hot gas desulfurization process. These sorbents can also convert the tars to compounds which will not crack and deposit coke on the electrodes of a molten carbonate fuel cell. Another sorbent has been identified for hot removal of the trace contaminants (sulfur and arsenic) present in coal gas to sub-ppm levels for MCFC applications.

The results obtained through efforts on these projects promise to show marked improvements in the development of advanced cleanup concepts for controlling and/or removing contaminants economically from coal-derived gas streams. Advanced research efforts will continue as well as efforts to determine the overall technical and economic feasibility of these concepts for possible future commercialization by the private sector. Successful eventual commercialization of cleanup unit operations using these concepts could provide advanced coal conversion/utilization system with emissions far below those seen from today's coal-fueled power systems.

## References

1. FY 85 Implementation Plan for the Gas Stream Cleanup Program, Gas Stream Cleanup Section, U.S. Department of Energy, Morgantown Energy Technology Center, August 20, 1984.
2. Benjamin, T. G., E. H. Camara, and L. G. Marianowski, "Handbook of Fuel Cell Performance," Prepared by Institute of Gas Technology for the U.S. Department of Energy, Contract No. EC-77-C-03-1545, May 1980.
3. Healy, H. C., et al., "Development of Molten Carbonate Fuel Cell Power Plant Technology," Quarterly Technical Progress Report No. 2, Prepared by United Technologies Corporation for the Department of Energy, Contract No. DE-AC01-79ET15440, August 1980.
4. Reinstrom, R. M., et al., "Development of Molten Carbonate Fuel Cell Power Plant," Quarterly Technical Progress Report for May-July 1980, Prepared by General Electric Company for the Department of Energy, Contract No. DE-AC02-80ET17019, September 1980.
5. Monitoring Contaminants in Coal-Derived Gas for Molten Carbonate Fuel Cells, "DOE/METC/82-44," Final Report by TRW, Prepared for Argonne National Laboratory, Contract No. 31-109-38-6108, May 1981.
6. Grindley, T. and G. Steinfeld, "Desulfurization of Hot Coal Gas by Zinc Ferrite," Prepared for Publication in "Acid and Sour Gas Treating Processes" by Gulf Publishing Company, June 1984.
7. Meyer, J. P. and M. S. Edwards, "Survey of Industrial Coal Conversion Equipment Capabilities: High-Temperature, High-Pressure Gas Purification," ORNL/TM-6072, Oak Ridge National Laboratory, June 1978.
8. High-Temperature Turbine Technology Program, FE-2290-27, Phase I, Program and System Definition, Topical Report, "Fuels Cleanup and Turbine Tolerance," Westinghouse Electric Corporation, February 1977.
9. Vidt, E. J., G. Jablonski, J. R. Hamm, M. A. Alvin, R. A. Wenglarz, and B. Patel, "Evaluation of Gasification and Gas Cleanup Processes for Use in Molten Carbonate Fuel Cell Power Plants," DOE/MC/16220-1306, Final Report, Westinghouse and Davy McKee for the U.S. Department of Energy, Morgantown Energy Technology Center.
10. "Protection of Environment," 40, Code of Federal Regulations, Parts 53 to 80, Office of the Federal Register, July 1, 1982.
11. Frumerman, R., "Gasification Cleanup Requirements," presented at the Second Annual Contractors' Meeting on Contaminant Control in Hot Coal-Derived Gas Streams, Morgantown, West Virginia, February 17 to 19, 1982.

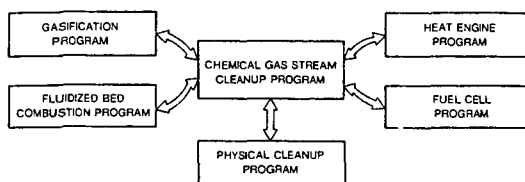


Figure 1. Cleanup Program Integration

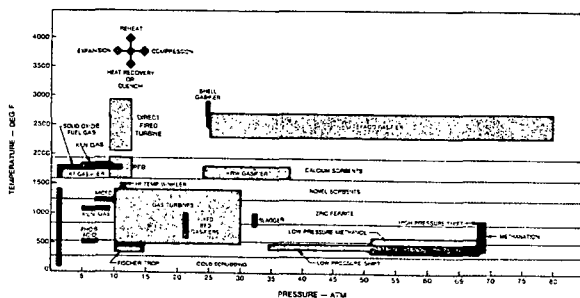


Figure 2. Temperature-Pressure Envelopes

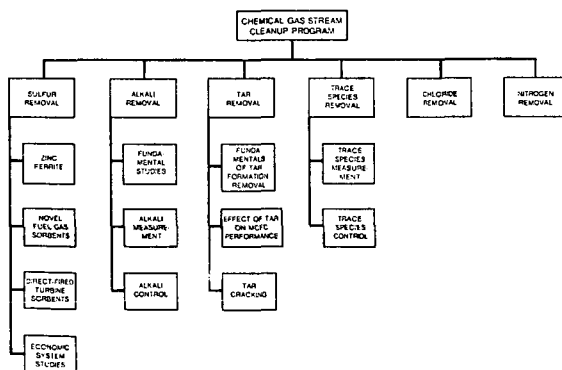


Figure 3. Chemical Gas Stream Cleanup Program

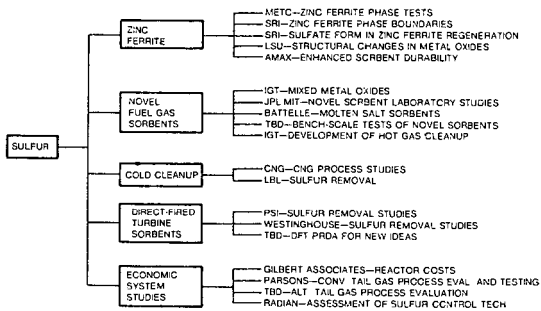


Figure 4. Sulfur Removal Projects

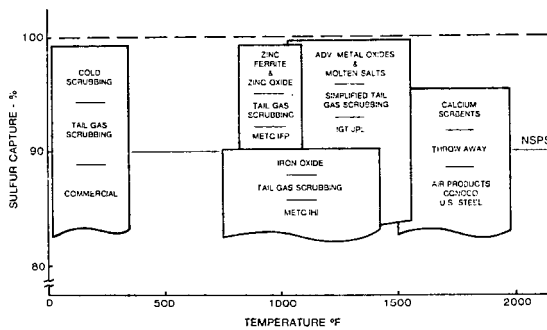


Figure 5. Fuel Gas Desulfurization

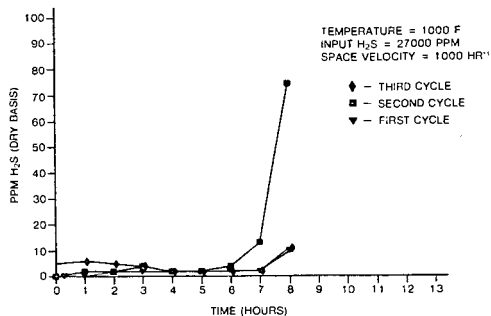


Figure 6. Zinc Ferrite Sulfidation

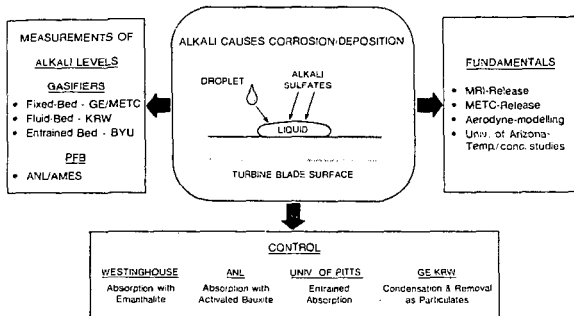


Figure 7. Alkali Removal Projects

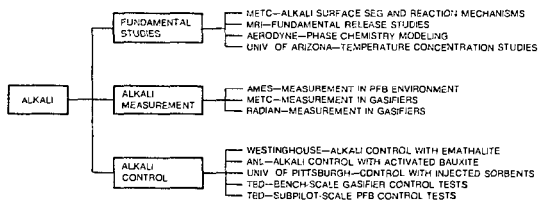


Figure 8. Alkali Removal Projects

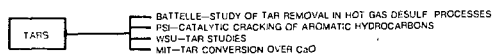


Figure 9. Tar Removal Projects

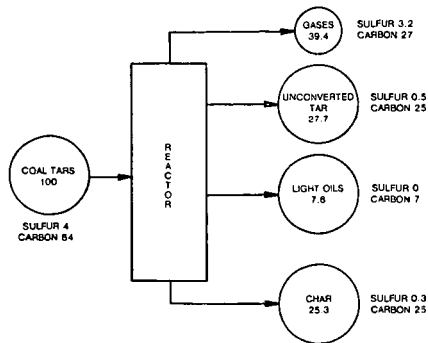


Figure 10. Catalytic Cracking of Coal Tars (Battelle-PNL)

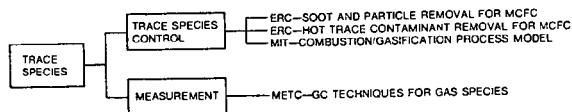


Figure 11a. Trace Species Removal Projects



Figure 11b. Chloride Removal Projects